ERDC/EL TN-12-2
May 2012

US Army Corps of Engineers®

Field Analysis of Munitions Constituents Using a Field-portable GC-MS

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PURPOSE: This technical note describes the use of a field-portable gas chromatograph (GC) mass spectrometer (MS) for the in-field analysis of munitions constituents (MCs) in groundwater. Field-portable instrumentation was used to analyze the explosives nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). Method performance was compared with that for a typical conventional laboratory method.

INTRODUCTION: The use of munitions constituents (MCs) at military installations can produce soil and groundwater contamination. Long-term monitoring programs at these sites often require periodic groundwater sampling. Conventional sampling and analytical techniques require shipping relatively large volumes of water to fixed laboratories that perform regulatory-approved analytical methods. Analysis and data reporting times for commercial analytical testing laboratories can be as long as 45 days (MacMillan and Splichal 2005). This process delays vital information about contaminant concentrations and incurs significant sample shipping costs. As groundwater is a dynamic system, the lag time between sample collection and data reporting can adversely affect the representativeness of the data. Additionally, most sample holding times have been established using a small "representative" set of environmental matrices. It is also assumed that analyte concentrations will not change significantly if analyzed within the holding time (typically 7 to 40 days) (Jenkins and Grant 1987; Jenkins et al. 1995a, 1995b). A field-portable GC-MS alleviates these concerns by providing near real-time data. While the ability to screen groundwater by direct sampling or solid phase micro extraction (SPME) has been tested, additional sample preparation and analysis options are desirable to ensure that in-field quantitation meets regulatory standards.

To provide scientifically defensible data for investigations and remedial efforts, the U.S. Army Engineer Research and Development Center (ERDC) has developed a field sampling and analysis plan to obtain definitive chemical data explosives in groundwater. The plan includes collecting and analyzing groundwater samples from actively monitored sites for a list of common, munitions-related contaminants: nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).

Previously the ERDC Environmental Chemistry Branch (ECB) deployed a Griffin 400 field-portable gas chromatography ion trap mass spectrometer (GC-MS) for the detection of MCs and PAHs (Bednar et al. 2009). This instrument was developed as part of the Environmental Quality and Installations Long Term Monitoring Program for field analyses of MCs in groundwater (Kirgan et al. 2008). The data quality was shown to be compromised by environmental factors

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1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
MAY 2012		**00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Field Analysis of Munitions Constituents Using a Field-portable GC-MS	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Engineer Research and Development Center (ERDC),3909 Halls Ferry Road,Vicksburg,MS,39180-6199**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**13**	

(e.g., heat and humidity) that negatively impacted the quality of the data. The stability of the portable Griffin 400 instrument was also an issue. Once the instrument was set up in the field, it was determined that the instrument needed to remain in a permanent location during analysis and downtime overnight in order to obtain optimum results.

The newer FLIR Griffin 450 addressed these issues, increasing the instrument stability and sensitivity. The data quality of the Griffin 450 was not observed to be compromised by heat and humidity. The temperature and relative percent humidity ranged from 65 to 90 °F (18-32 °C) and <55 to 85, respectively, during the Griffin 450 field tests. As MCs are commonly determined in the laboratory using GC-ECD by U.S. Environmental Protection Agency (EPA) Method 8095 or GC-MS following Method 529 (USEPA 2002, 2007), only minor modifications to the explosives detection method (temperature program, gas flows, etc.) were required for the field method to detect MCs.

To collect samples and perform in-field analyses, the investigative team (which consisted of ERDC and FLIR personnel) deployed to the Louisiana Army Ammunition Plant at Minden, LA (LAAP) for 3 days during March 2010; and to the Milan Army Ammunition Plant at Milan, TN (MAAP) for 5 days during April 2010. The team collected water samples from 10 of the monitoring wells in Area P of the LAAP, and 18 of the monitoring wells at the MAAP during its routine long-term monitoring operations. Samples were prepared and analyzed in the field. Sample splits were stored in coolers at 4 ^{o}C and sent to the Environmental Chemistry Laboratory in Vicksburg for comparative analysis by HPLC using USEPA Method 8330B (U.S. Environmental Protection Agency (USEPA) 2006).

MATERIALS AND METHODS:

Groundwater collection. Twenty-eight samples were collected from conventionally installed monitoring wells at two military installations (the LAAP and MAAP).

Water samples were collected from 10 monitoring wells at Area P of the LAAP and 18 monitoring wells at the MAAP for the analysis of NB, 1,3-DNB, 2,4-DNT, TNB, TNT, and RDX. Groundwater samples were collected in 4-L amber jugs that were shielded from light and stored on ice to prevent degradation of the analytes. The 4-L samples were split into 1-L aliquots for field and traditional laboratory analyses. The first aliquot of each sample was analyzed in the field with the field-portable GC-MS; the second aliquot was shipped to a laboratory and analyzed by HPLC-UV by Method 8330B (USEPA 2006). The two remaining 1-L aliquots were reserved for analysis in case of breakage during transport or for the preparation of field and laboratory QC samples (e.g. duplicates and matrix spikes). ERDC personnel collected the groundwater samples at the LAAP using dedicated Teflon tubing. Wells at the LAAP were sounded to determine the groundwater depth before the sampling pump was deployed. A stainless steel submersible pump was placed at the midpoint of the screened interval. Groundwater samples were collected after the pH, conductivity, dissolved oxygen, temperature and turbidity stabilized, as monitored with a field meter (YSI 556 MPS Multi probe system, YSI environmental, Yellow Springs, OH). This ensured formation water samples were collected. The wells were pumped at the lowest flow rate setting to prevent pumping the wells dry. Well water samples at the MAAP were collected by Arcadis U.S., Inc. (2849 Paces Ferry Road, Suite 400, Atlanta, GA 30339) as part of normal monitoring activities at the site. A minimum of three well volumes were discharged from the wells before sample

collection. During discharge, temperature and pH were monitored; sample collection occurred after these parameters stabilized.

Samples for traditional laboratory analysis were collected, stored and shipped under chain of custody in a manner that minimized degradation of the munitions constituents (e.g., the samples were packed on ice and stored in the dark). Each sample was labeled to identify the site, well number, and time and date of collection. Laboratory extracts and analyses were performed within standard method holding times.

Field extraction techniques. Three to six wells per day were evaluated. Analytes were extracted from the aqueous samples prior to analysis using solid phase extraction (SPE) cartridges (Porapak RDX, Waters, 34 Maple Street, Milford, MA) following USEPA Method 3535A (USEPA 1996). The SPE cartridges were conditioned in the laboratory by eluting 15 mL of acetonitrile followed by 15 mL of DI water. They were stored on ice in a sealed Ziploc bag and shielded from light until needed. Depending on the expected concentrations of the munitions constituents, 0.05- to 1.6-L sample volumes were extracted, as overloading the SPE cartridges can result in analyte breakthrough. The groundwater was drawn through the SPE cartridge at a rate of < 20 mL per minute. The MCs were eluted from each SPE cartridge with 5 mL of acetonitrile and collected in a 15-mL centrifuge tube. Extracts were brought to a final volume of 5 mL, mixed thoroughly and then transferred to a 10-mL amber vial. The laboratory control and matrix spike samples were spiked with 5 uL of 1000 mg/L 8330 mix A, and extracted off an SPE cartridge in the same manner. Concentration factors of 10 to 320 for the samples produced concentrations in the final extracts that were within the GC-MS calibration ranges (approximately 0.3 - 3.5 mg/L). A 1-mL aliquot was then transferred to a 1.5-mL amber vial, dried with sodium sulfate, and spiked with 5 μL of the internal standard 3,4-DNT to obtain a final concentration of 5 mg/L.

Field GC-MS analysis. The instrument used for all field analyses was a Griffin (West Lafayette, IN) 450^{TM} gas chromatograph with a cylindrical ion-trap mass spectrometer (Kirgan et al. 2008). The system is shown in Figure 1. Three to six groundwater samples, along with the required QC spikes and duplicates, were analyzed each day during field operations. Instruments were calibrated

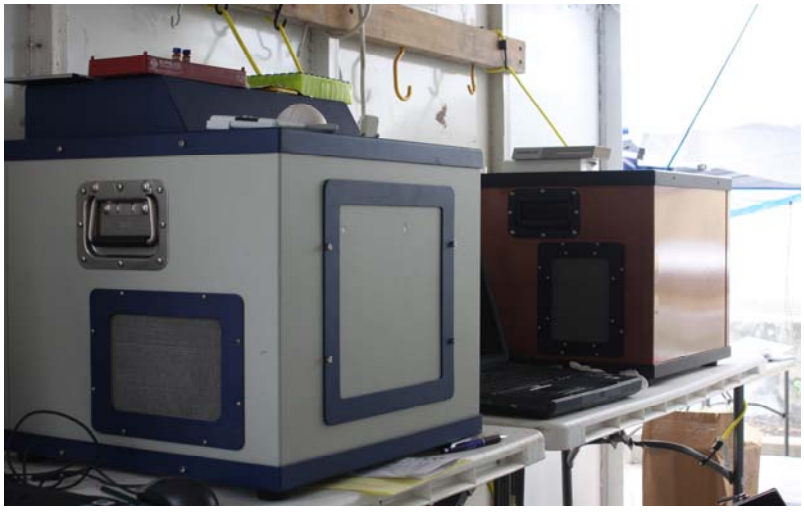

Figure 1. Field-portable Griffin 450 GC-MS instrument setup as deployed at LAAP and MAAP.

while the groundwater samples were collected and extracted. Analysis by GC-MS of the SPE extracts commenced once the calibration curve had been determined and a verification standard had been analyzed. Calibration verification standards were analyzed periodically to confirm instrument calibration. Samples and standards were analyzed on the GC-MS by injecting 1-μL volumes onto the column (5 m Restek-TNT II).

The operational conditions of the GC-MS are as follows: The injection inlet is maintained at 200 ^{o}C with a constant helium carrier gas flow of 1 mL/min. The column temperature profile begins at 40 ^{o}C, is held for 1.5 minutes, and is then ramped to 135 ^{o}C at a rate of 30 ^{o}C/min. The rate is then adjusted to 50 ^{o}C/min to a final temperature of 280 ^{o}C, which is held for 2 minutes for column bake-out. The run time for the entire temperature program and data collection is approximately 9 minutes. The GC profile was such that the contaminants of interest were chromatographically resolved. Selected ion monitoring (SIM) mode is used to detect a standard list of ions for the MCs of interest (Table 1). Mixed analyte calibration standards were purchased from Restek and used to calibrate the instrument from 300 to 3,500 μg/L. A minimum of six analyte concentrations (ranging from 0.4 to 3.5 mg/L), each containing 5 mg/L of 3,4-DNT as an internal standard to correct for instrumental drift, were evaluated. Linear response functions were obtained for each analyte (Figure 2, Table 2), and typically had correlation coefficients greater than 0.95. Figure 3 is a chromatogram of a mixed (Restek) standard (2500 μg/L) that was analyzed in the field by this technique. Figure 4 is a chromatogram of a groundwater sample from MAAP. The groundwater sample contained three detectable contaminants: TNB (0.0052 mg/L), TNT (0.0788 mg/L), and RDX (0.0042 mg/L).

The reporting limits were determined based on the lowest calibration standard. The lowest initial calibration standard was 300 μg/L. An extraction process concentration factor of 320 results in quantifiable aqueous concentrations of 1 - 2 μg/L. A 1-μg/L water sample was extracted to verify the reporting limit.

Field analysis results. Table 3 lists groundwater concentrations determined in the field using the Griffin 450 GC-MS for the LAAP and the MAAP. Laboratory control (LCS and LCSD) and matrix spike (MS and MSD) samples were analyzed each day as batch QC samples.

As shown in Table 4, most of the spike recoveries fell within the acceptance limits of the DoD Quality Systems Manual (QSM). Some of the non-compliant LCS recoveries likely occurred because the sample extracts were not thoroughly dried prior to injection. Matrix spike recoveries were within DoD QSM acceptance limits for NB, 1,3-DNB, 2,4-DNT and TNT for all days except day 2 at the LAAP. The well sample for day 2 at the LAAP was highly contaminated and the spike was insignificant to the MCs present in the well except for NB, which was not present in the matrix water. RDX recoveries were within DoD QSM limits in 57% of the LCS control samples and were consistently low for the matrix spike samples, which is characteristic of performance issues often encountered for GC analyses of RDX.

Table 1. FLIR Griffin 450 SIM retention times and monitored ions.

Metrics	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
Retention Time	1.43	3.65	4.03	4.55	4.59	5.0
Ion Monitored	123	167	165	213	210	128

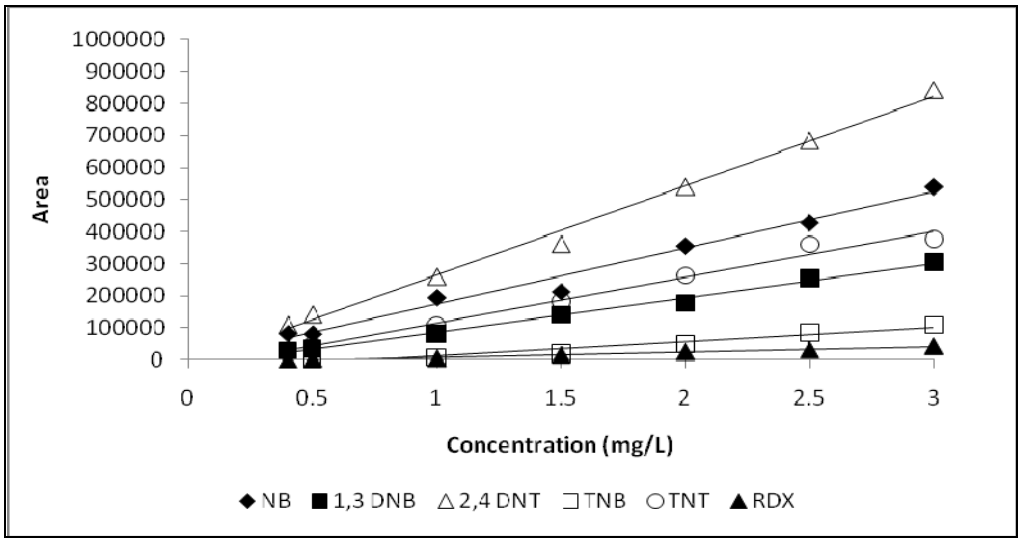

Figure 2. Calibration curves for NB, 1,3-DNB, 2,4-DNT, TNB, TNT and RDX.

Table 2. Calibration curve data parameters.

Analyte	Quantitation Mass Monitored, (*m/z*)	Retention Time (minutes)	Calibration Curve[1, 2]	R^2
NB	**123**	**1.43**	**C=(A-90.48)/174516.95**	**0.98**
1,3-DNB	**167**	**3.65**	**C=(A+19849.76)/106797.08**	**0.99**
2,4-DNT	**165**	**4.03**	**C=(A+12325.51)/278102.7**	**0.99**
TNB	**213**	**4.55**	**C=(A+32385.71)/44806.29**	**0.95**
TNT	**210**	**4.59**	**C=(A+29116.76)/143635.9**	**0.99**
RDX	**128**	**5.00**	**C=(A+7259.44)/15834.53**	**0.98**

[1]C is the concentration of the analyte and A is the area of the quantitation masses monitored.
[2]Calibration curve data were collected in the field at MAAP.

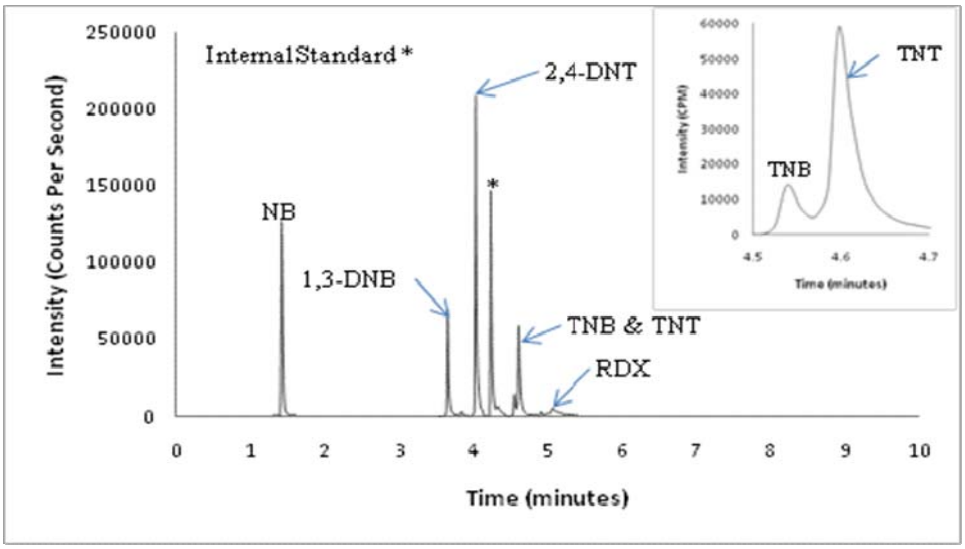

Figure 3. Reconstructed ion chromatogram of a 2500-μg/L munitions standard analyzed with the Griffin 450 GC-MS. The internal standard compound (3,4-DNT) is labeled with "*", MCs compounds are also indicated. Only the SIM ion scans are shown.

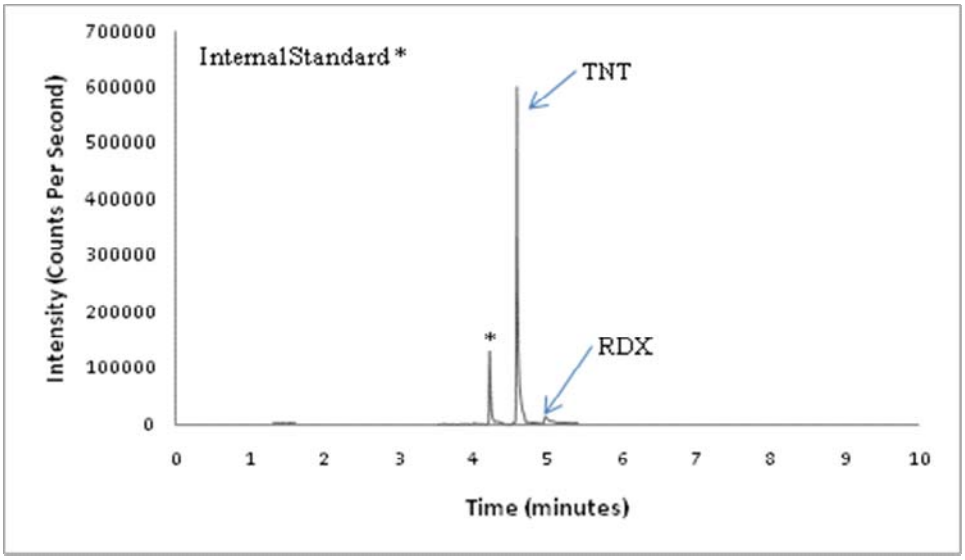

Figure 4. Reconstructed ion chromatogram of a groundwater sample from the MAAP analyzed with the Griffin 450 GC-MS. The internal standard compound is labeled with "*", MCs compounds are also indicated. Only the SIM ion scans are shown.

Table 3. FLIR Griffin 450 results for wells at LAAP and MAAP. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0178	0.0107	0.0643	1.1542	0.7663	3.1228
111	<0.0016	0.0009	<0.0007	0.0031	0.0015	<0.0006
112	<0.0015	0.0011	0.0007	0.0030	0.0027	0.0292
105	<0.0356	0.0407	0.0227	1.0887	0.1939	0.1939
104	<0.0356.	0.2980	0.1678	12.5725	6.7263	17.9812
140	<0.0089	0.0846	0.0355	0.0283	0.8421	1.9238
141	<0.0089	0.1059	0.1002	1.5073	1.1937	0.6502
142	<0.0015	<0.0006	<0.0007	0.0033	0.0008	0.0029
85	<0.0356	<0.0133	0.0256	10.2946	2.0208	2.8327
110	<0.0178	<0.0067	<0.0080	0.0594	0.0376	0.0442
MI660	<0.0036	<0.0013	<0.0016	<0.0006	0.0289	0.0285
MI658	<0.0030	0.0025	0.0017	0.0081	0.0977	0.0890
MI653	<0.0015	0.0010	<0.0007	<0.0002	0.0018	0.0040
MI645	<0.0015	<0.0006	<0.0007	<0.0002	0.0012	0.1384
MI531	<0.0011	<0.0004	<0.0005	<0.0002	0.0010	0.0030
MI570	<0.0045	<0.0017	<0.0020	<0.0007	0.0054	0.0091
MI533	<0.0011	<0.0004	<0.0005	<0.0002	0.0188	0.0680
MI536	<0.0018	<0.0007	<0.0008	0.0042	0.0028	0.0368
MI537	<0.0015	<0.0006	<0.0007	0.0037	0.0084	0.0146
MI538	<0.0015	<0.0006	<0.0007	0.0035	0.0127	0.0155
MI654	<0.0018	<0.0007	<0.0008	0.0282	0.0181	0.0367
MI355	<0.0011	<0.0004	<0.0005	0.0019	0.0012	0.0285
MI514	<0.0018	<0.0007	<0.0008	0.0052	0.0788	0.0042
MI516	<0.0018	<0.0007	<0.0008	0.0032	0.0094	0.0016

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
MI534	<0.0011	<0.0004	<0.0005	0.0020	0.0021	0.0133
MI569	<0.0011	<0.0004	0.0005	0.0022	0.0008	0.0015
MI571	<0.0011	<0.0004	<0.0005	<0.0002	0.0008	0.0014
MI573	<0.0011	<0.0004	0.0006	0.0023	0.0309	0.0708

Table 4. FLIR Griffin 450 LCS and MS % recoveries. Bolded values are outside DoD QSM limits.

Location/Day	Sample ID	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
DoD QSM Limits		50-140	45-160	60-135	65-140	50-145	50-160
LAAP Day 1	LCS	78	73	82	83	74	57
	LSD	61	64	63	78	62	**44**
LAAP Day 2	LCS	58	47	60	73	59	**33**
	LSD	**43**	**38**	**41**	**61**	**41**	**NR**
LAAP Day 3	LCS	110	65	96	91	83	69
	LSD	110	100	91	100	93	**49**
MAAP Day 1	LCS	100	98	91	81	82	55
	LSD	91	100	110	89	90	64
MAAP Day 2	LCS	110	93	100	72	67	**41**
	LSD	130	93	100	**55**	56	**39**
MAAP Day 3	LCS	99	100	110	**62**	70	57
	LSD	160	100	110	**56**	64	61
MAAP Day 4	LCS	77	110	100	79	88	110
	LSD	110	120	120	100	84	50
LAAP Day 1	111MS	96	86	91	74	63	**45**
	111MSD	100	74	120	100	92	**38**
LAAP Day 2*	104MS	92	**27**	84	**750**	**490**	**-2200**
	104MSD	99	87	111	**-1000**	**-900**	**-3800**
LAAP Day 3	142MS	80	72	73	75	72	54
	142MSD	96	100	93	88	81	**49**
MAAP Day 1	531MS	120	110	110	66	55	**9.8**
	531 MSD	120	77	96	79	58	**26**
MAAP Day 2	536MS	110	68	100	**59**	54	**260**
	536 MSD	120	99	120	89	81	**200**
MAAP Day 3	355MS	**160**	110	110	**22**	61	**20**
	355MSD	140	93	110	**23**	66	**37**
MAAP Day 4	569MS	70	99	94	66	86	**33**
	569MSD	98	130	100	76	96	**34**

Laboratory HPLC analysis. The fixed-laboratory analyses were conducted using an Agilent (Palo Alto, CA) 1200 HPLC equipped with Phenomenex Synergi 4-µm hydroRP (80A 250x4.6mm) and Restek Pinnacle II biphenyl (5µm 150x4.6mm) reverse-phase columns at the U.S. Army Engineer Research and Development Center for samples from the LAAP and the MAAP. The latter reverse-phase column was used for analyte confirmation. Analytes were detected with UV absorbance at 254 nm following Method 8330B (USEPA 2006). The operational

conditions for the HPLC are as follows: injection volume 50mL, isocractic elution at 0.9mL/min utilizing 45:51:4 methanol:water:acetonitrile as the mobile phase, UV absorbance 254 nm, and autosampler and column temperatures of 10 ^{o}C and 25 °C, respectively.

Laboratory analysis results. Table 5 lists the LAAP and the MAAP groundwater concentrations as determined by HPLC at the Environmental Chemistry Branch laboratory in Vicksburg, MS. The analyte extraction efficiency has been shown to be the same for both the fixed-laboratory method and the field method (Kirgan et al. 2008). The concentration factors for the field and the laboratory analyses were also the same, as the same sample and final volumes were used for both extraction methods. The analyte concentrations measured by the laboratory and field methods qualitatively agree. The laboratory and field results for all of the detected MCs in groundwater are plotted in Figure 5, showing generally good agreement (slope ≈ 0.95) between the two techniques below a concentration of 10 mg/L (Figure 5, right). Concentrations above 10 mg/L significantly bias the results, resulting in an overall observed slope of about 1.31 (Figure 5, left).

Table 5. HPLC laboratory results (mg/L) for groundwater samples at LAAP and MAAP.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0005	0.0082	0.0738	0.7259	0.6142	2.0165
111	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
112	<0.00004	0.0003	0.0011	0.0003	0.0004	0.0248
105	<0.0010	0.0340	0.0093	0.7398	0.2231	0.2231
104	<0.0010	0.3286	0.1901	8.2453	6.5697	13.6107
140	<0.00025	0.0834	0.0372	0.0234	0.7790	2.9515
141	<0.00025	0.0311	0.1009	1.1211	1.2344	0.7841
142	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004
85	<0.0010	0.0029	0.0247	6.7785	1.7333	4.0635
110	<0.0005	0.0461	0.0710	0.3817	0.6814	4.2326
MI660	<0.0001	<0.0001	0.0004	0.0007	0.0398	0.0681
MI658	<0.00008	0.0001	0.0009	0.0009	0.0958	0.1426
MI653	<0.00004	<0.00004	0.0001	0.0001	0.0011	0.0045
MI645	<0.00004	<0.00004	0.0002	0.0001	0.0004	0.2103
MI531	<0.00003	<0.00003	<0.00003	0.0001	0.0009	0.0011
MI570	<0.0001	<0.0001	<0.0001	0.0004	0.0047	0.0076
MI533	<0.00003	0.0001	0.0003	0.0008	0.0225	0.0711
MI536	<0.00005	<0.00005	0.0002	0.0002	0.0034	0.0348
MI537	<0.00004	<0.00004	0.0001	0.0035	0.0349	0.0341
MI538	<0.00004	<0.00004	0.0001	0.0018	0.0321	0.0700
MI654	<0.00005	<0.00005	0.0004	0.0006	0.0103	0.0755
MI355	<0.00003	<0.00003	<0.00003	0.0001	<0.00003	<0.00003
MI514	<0.00005	<0.00005	0.0003	0.0068	0.0857	0.0097
MI516	<0.00005	<0.00005	0.0001	0.0004	0.0160	0.0206
MI534	<0.00003	<0.00003	<0.00003	0.0004	0.0032	0.0026
MI569	<0.00003	<0.00003	<0.00003	0.0001	0.0001	0.0003
MI571	<0.00003	<0.00003	<0.00003	<0.00003	0.0001	0.0001
MI573	<0.00003	<0.00003	0.0002	0.0003	0.0037	0.0048

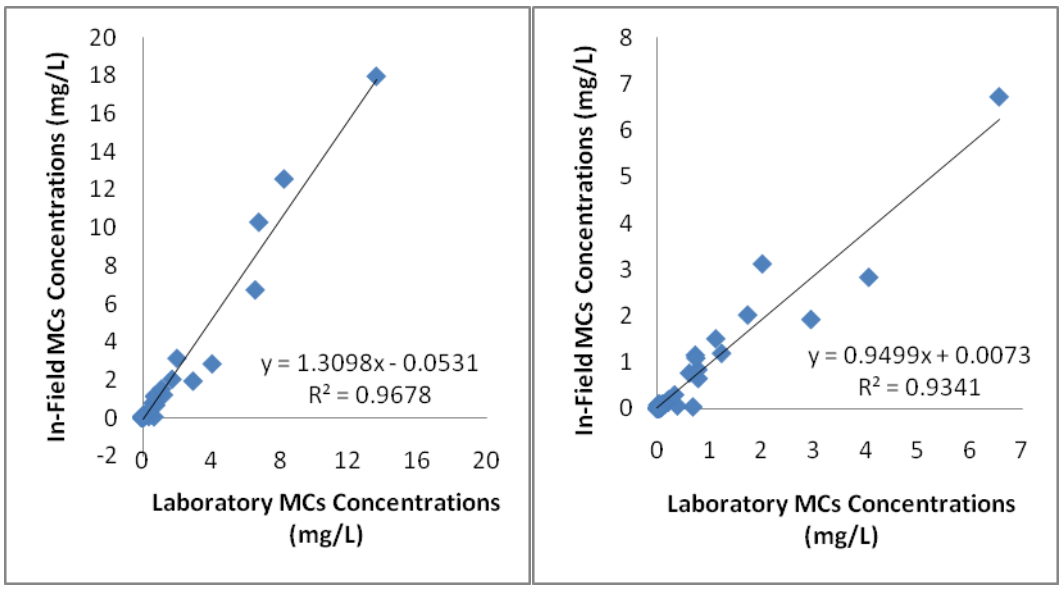

Figure 5. Comparison of field and laboratory MCs concentration data for groundwater samples. Left graph shows the linear regression fit for the complete data set. The graph on the right shows the linear regression fit of data under 10 mg/L.

Graphical analysis of the plots of the Griffin field data versus the HPLC laboratory data for the individual MCs of interest show linear regression slope values between 0.80 and 1.20 for 1,3-DNB, 2,4-DNT and TNT (Table 6). Nitrobenzene (NB) was not detected in any of the groundwater samples. Therefore, only comparisons of non-detects and evaluations of spike recoveries were possible. The linear regression comparison of the field results with conventional fixed-laboratory results for RDX resulted in a slope of approximately 1.3. However, if only concentrations below 10 mg/L are considered, the resultant slope is approximately 0.79. The truncated slopes (Table 6) were calculated from data pairs below a concentration of 10 mg/L. However, only TNT had data pairs above 5 mg/L. SPE of groundwater samples containing >3 mg/L result in final solution concentrations above the linear dynamic range of the instrument (0.4-3.5 mg/L) and thus must be diluted before GC-MS analysis. Trinitrobenzene exhibited slopes that did not fall within the target range of 0.8–1.2.

Table 6. Slopes from linear regression analysis of Griffin 450 results vs. traditional HPLC results for individual MCs.

Data Set	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
Slope complete data set	N.A.	0.86	0.88	1.5	1.0	1.3
Slope of Truncated data	N.A.	0.86	0.88	1.4	1.0	0.7

Statistical comparison of field and laboratory data. The compounds NB, 1, 3-DNB, 2, 4-DNT, TNB, TNT, and RDX were evaluated. Split groundwater samples were collected and analyzed for these compounds to compare the results from a field-portable GC-MS method (denoted by the variable *F*) to the results from a conventional fixed laboratory method (denoted by

the variable *L*). Parametric and non-parametric linear fits were preformed for the remaining five compounds. The regression line data in Table 5 demonstrate that the slopes are within the 0.8 to 1.2 limit except for TNB and RDX. However, the TNB data were skewed somewhat by two samples with high concentrations. A similar effect was observed for RDX with one sample skewing the results. These samples reflect the linear dynamic range limitations of the current instrument. When large sample pre-concentration factors result from the SPE procedure, the data can fall outside the linear dynamic range of the field instrument. Truncated sample data sets (below 5 mg/L, for instance) show that there are ranges where the data are comparable to the laboratory results. See Table 7 below, where *F* corresponds to Griffin field data and *L* corresponds to laboratory HPLC data.

Table 7. Statistical analyses comparing the field (F) and laboratory results (L).

Compound	Kendall Equation	OLS Equation	Relationship	Remarks
NB	N/A	N/A	N/A	Agreement between non-detects
1, 3-DNB	F=1.01L+0.000	F = 0.86L+0.018	$F \approx L$	$F \leq 0.3$ ppm
2, 4-DNT	F=0.94L+0.0004	F = 0.88L+0.0034	$F \approx L$	$F \leq 0.2$ ppm
TNB	F=1.34L+0.002	F= 1.5L - 0.026	F = 1.5 L	$0.05 \text{ ppm} \leq F \leq 10$ ppm; $F < 0.05$- Screening-level
TNT	F=0.87L+0.0007	F = 1.0L - 0.013	$F = L$	$0.05 \text{ ppm} \leq F \leq 10$ ppm; $F < 0.05$ - Screening-level
RDX	F=0.69L+0.001	F = 1.3L - 0.11	$F \approx 0.7$ L	$F \leq 1$mg/L - Screening-level only

The field method for RDX possessed a negative bias relative to the fixed-laboratory method and exhibited relatively large variability across all concentration ranges evaluated. The field results were about 70% of the laboratory results on the average for concentrations < 1 mg/L. The evaluation was conservatively limited to RDX concentrations < 1 mg/L because RDX was detected at a larger concentration (10 mg/L) for only one sample. There was variable quantitative agreement for RDX in the individual split samples, yet there was excellent qualitative agreement between the field and laboratory results. Therefore, it is suggested that the field method produces screening level data only for RDX. As indicated by the large slope (1.5), the field method exhibits a significant positive bias for TNB, (The bias was also observed from the sign test, Prentice-Wilcoxon test, and box plots). There was a very strong correlation between the laboratory and field methods for concentrations greater than about 0.05 mg/L to the highest reported concentration, but the performance of the field method was relatively poor at smaller concentrations. Much of the positive bias may be attributed to the poor chromatographic resolution of TNB and TNT and the similar mass spectra produced by these two compounds. Most of the groundwater samples tested had TNT concentrations that were at least an order of magnitude greater than TNB; the high TNT concentrations may have resulted in erroneously high TNB values for the field technique.

APPLICABILITY: The field-portable instrumentation described above has the capability to analyze for a wide variety of organic contaminants in complex environmental matrices. The Griffin 450 GC-MS weighs approximately 44 kg, has dimensions of approximately 48.8 × 48.8 × 53.6 cm, and can be operated on a 2-kW portable generator. The instrument can be deployed to any environment where this space and power are available. The work discussed above was specifically focused on explosives. However, the technology can be modified to analyze for a wide variety of organic compounds. For example, during the instrumentation's original prove-out deployment for MCs in groundwater analysis, an unknown chromatographic peak in certain monitoring wells was identified as a plasticizer compound because of the mass spectrometer's ability to detect and identify organic molecules based on their molecular weight and structure (Figure 6). Additionally, GC-MS is routinely used to analyze for petroleum hydrocarbons and polycyclic aromatic hydrocarbons; therefore, this field technique can be extended to other classes of organic compounds, including polychlorinated biphenyls and pesticides (Bednar et al. 2009).

SUMMARY: The use of a field-portable GC-MS was described for the near-real-time analysis of MCs in groundwater. The field and laboratory NB results were consistent in that both the field and laboratory methods reported non-detects for NB for all of the split sample analyses. The field method for RDX possessed a negative bias relative to the fixed laboratory method and exhibited relatively large variability across all concentration ranges evaluated. The field results for RDX were about 70% of the laboratory results on the average. However, there was excellent qualitative agreement between the field and laboratory results. The field method consistently exhibited a significant positive bias for TNB. There was a very strong correlation between the laboratory and field methods for concentrations greater than about 0.05 ppm to the highest reported concentration, but the performance of the field method was relatively poor at smaller concentrations. There was good quantitative agreement between the field and laboratory methods for 1, 3-DNB and 2, 4-DNT for the low concentration ranges that were evaluated. There was also excellent quantitative agreement between the field and laboratory methods for TNT in the concentration range from 0.05 ppm to 10 ppm.

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This study was conducted under the Environmental Security Technology Certification Program, (ESTCP Project No. ER-0922). This technical note should be cited as follows:

> Bednar, A.J., M. Wells, A.L. Russell, C.A. Hayes, W.T. Jones, P. Tackett, D. Justes, R.A. Kirgan, D. Splichal, L. Parker and T. Georgian. 2012. *Field analysis of munitions constituents using a field-portable GC-MS.* ERDC Technical Notes Collection (ERDC/EL TN-12-2). Vicksburg, MS: U.S. Army Engineer Research and Development Center.

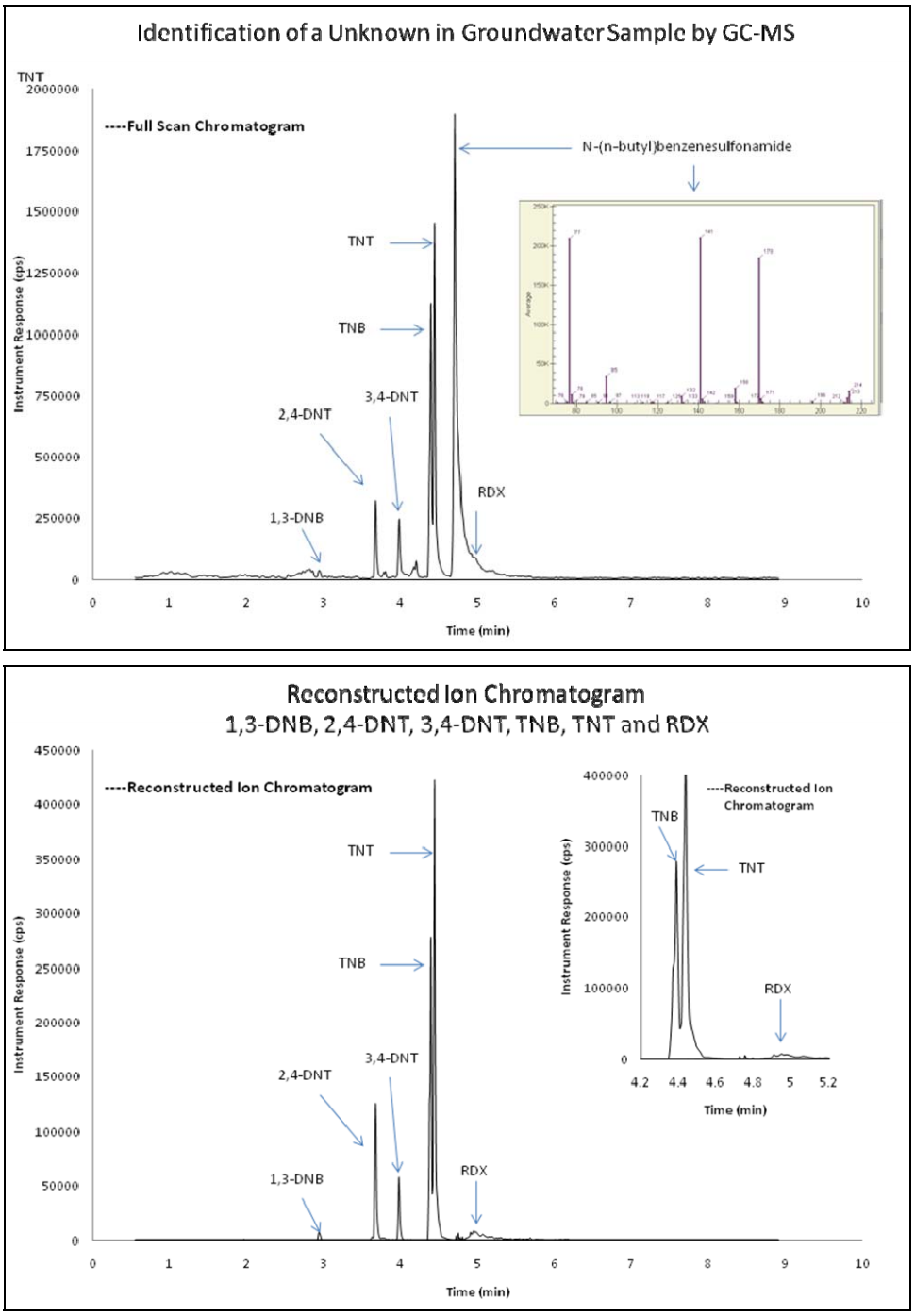

Figure 6. Full scan chromatogram of SPE-extracted groundwater sample (top) containing a plasticizer interferent. RDX appears as a shoulder on the right side of the plasticizer peak. The RDX peak is not resolved in the total ion chromatogram, but is clearly defined in the reconstructed ion chromatogram (bottom). The retention time shift (compared to Figures 2 and 3) is due to slight temperature program adjustments made during field analysis and testing, including an increased starting temperature (80 °C rather than 40 °C).

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